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(54) Title: CLAY MINERALS

(57) Abstract

A litter box is charged with a flowable granular composition convertible in contact with a small water addition to agglomerates readily dispersible in a charge water addition, comprising at least one water-swellable clay mineral and at least one hydrophilic non-clay component additional to any alkali bound to the clay. Preferably the non-clay component is selected from the group consisting of a non-surfactant water-soluble material, a water-soluble surfactant, and a finely divided water-insoluble material. The invention also provides the aforementioned composition in which the non-clay component is present as solid particles adherent to the exterior of the clay particles, and a process of making the composition.

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CLAY MINERALS

This invention relates to clay minerals and in particular to a clay mineral composition and its use in handling body waste products.

In handling such a product, for example blood, urine, vomit and faeces of animals, it has been proposed to deposit it on a litter of water-absorbent clay, whereby the clay agglomerates locally, and then to remove and dispose of the litter agglomerate. Especially when the product may contain noxious microorganisms, for example toxoplasmosis, it is important to remove the agglomerate positively from human contact, to avoid setting up a cycle of infection. Disposal would be desirably by way of the sewerage system, but only if the agglomerate is readily and permanently dispersible in water so as not to block the system.

In US-A-5000115 it is proposed to use as litter particles having a size ranging from about 60 microns to about 3350 microns of water-swellable bentonite clay capable of agglomerating upon local wetting into a mass physically removable from unwetted litter. In EP-A-0424001 it is disclosed that agglomerated litter comprising a combination of sodium bentonite and calcium bentonite in defined proportions can be disposed of through a household plumbing line without clogging it. I have now identified an absorbent composition, at least some forms of which I believe to

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be new <u>per se</u>, and which is very effective in agglomeration in contact with waste products and (at least in preferred forms) in subsequent disposal by dispersion in water.

In this specification all percentages are by weight.

According to the invention a litter box is charged with a flowable granular composition convertible in contact with a small water addition to agglomerates readily dispersible in a large water addition comprising at least one water-swellable clay mineral and at least one hydrophilic non-clay component additional to any alkali bound to the clay.

Typically said component is at least one of a nonsurfactant water-soluble material, a water-soluble
surfactant and a finely divided water-insoluble
material. It is preferably non-polymeric but may be
for example a low polymer having up to about 20
repeating units, so as to provide for ready solubility
in water.

I believe the non-clay component functions by setting up zones of weakness and/or water-accessibility in the agglomerates, thus facilitating dispersion in presence of a large water addition. Thus the invention may be defined in terms of a clay composition in which the balance between cohesiveness and redispersibility is adjusted in favour or redispersibility by inclusion of the said non-clay component.

products.

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The invention provides also:

the composition <u>per se</u> so far as it is novel;

processes of making the composition;

a process of handling water-wet animal waste

The clay mineral (referred to hereinafter as clay) should be rapidly swollen by water, suitably to 5-10ml water per g within 3 minutes, to a coherent gel. It is thus preferably non-calcined. It can consist substantially of any smectite clay, for example bentonite or montmorillonite, or possibly attapulgite, beidellite, fuller's earth, hectorite, nontronite, saponite or sepiolite. Whereas it may contain calcium bentonite and may thus benefit from the resulting previously published redispersibility, it preferably does not to any substantial extent for example over (This is additional to any calcium bentonite notionally present as calcium ions in the clay ingredient of the composition or in the non-clay component). Thus the manufacturing complication of feeding two types of clay are avoided. preferably at least partly in its alkali metal form, since alkaline earth clays are less swellable. Preferably the clay of the composition is over 50, more preferably over 65, especially over 80, % sodium bentonite. There may be a few percent of other minerals such as quartz, cristobalite, iron or titania present, but these do not affect the operation of the

invention and may indeed assist by providing hydrophilic finely divided material.

The granules can be of any convenient size. For cat litter they are preferably to the extent of at least 90% in the range 0.2 to 4.0mm, especially 0.3 to 2.0mm. The granule size is less important for static uses such as in birdcages, slaughter or surgery.

In the granules the clay and non-clay component(s) should be closely associated together, since this appears to assist dispersion in the larger addition of water. Some or all of the non-clay component can be within the interstices of the clay particles. It is preferred to have the non-clay component, especially if it is a salt, present as solid particles adherent to the exterior of the clay particles. The composition having this structure is believed to be novel per se.

The clay is capable of a range of relevant properties dependent on which species of clay is used, where it is mined and what if any physical treatment it undergoes in preparing it for use. Thus, in addition to possible treatments to concentrate the required clay, it may for example be:

- non-compacted, as the product of simple drying on a belt; or
 - 2. compacted by compression; or
 - 3. granulated by wet extrusion and cutting.

In each case there may be stages of drying and/or grinding and/or sieving. Preferably the clay is at

least partly, for example at least 50%, the product of wet extrusion.

The clay component may be an opened clay mineral, that is, one that has been subjected to treatment, typically in presence of water, in shearing conditions. It is believed that such treatment partly disrupts the layer structure of the clay. Preferably such treatment is in presence of mild alkali, for example sodium carbonate 0.5 to 5.0% on dry clay. The quantity of water present should be enough to make the clay workable, but short of full swelling of the clay. The clay raw material may be wet clay as mined. The treatment preferably includes extrusion through a perforated plate.

To make such a preferred clay, raw sodium bentonite may be activated with soda ash and milled in a pan muller, in which it is extruded through slots in the pan floor. It is then dried and screened. Such extrusion exposes the bentonite to efficient activation and makes a homogenised processed product.

Conveniently only alkali carbonate is added at this stage, other non-clay component(s) being added later.

A very suitable clay is one intended as a soil sealant for earth dams, for example the granulated sodium bentonite available under the trade name CULSEAL from SAMREC Pty Ltd, of Olifantsfontein, RSA.

The clay component can be one or more rendered more swellable by kneading with an alkali metal

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compound, for example those described in:

EP-A-603773: weakly swelling bentonite (40-65% montmorillonite or calcium bentonite) kneaded with sodium carbonate;

EP-A-604860: smectic clay reacted with sodium-form ion exchanger such as zeolite; and

EP-A-604861: low-swelling smectite such as calcium smectite or two-layer silicate such as kaolin kneaded with alkali smectite.

The non-clay component can be any that affords flowable particles when mixed with the clay. It can be organic, for example a sugar or viscous hydroxy compound, or possibly urea. Most conveniently it is or includes one or more salts.

Such salt preferably has a solubility of at least 4, especially at least 20, g per 100ml of water at ambient temperature. It has the anion preferably of an acid dissociation at least as strong as acetic acid. The pH of its molar aqueous solution is preferably in the range 5-9. Examples of usable salts, from among which uni-univalent salts are preferred, are the acetate, bromide, carbonate, chloride, citrate, nitrate, hydrogen-phosphate and sulphate of sodium and/or potassium; other examples are complex salts such as sodium ammonium phosphate, potassium calcium chloride, potassium aluminium sulphate, naturally-occurring complex salts comprising any of those mentioned; also ammonium salts such as the chloride,

nitrate or sulphate; and also magnesium sulphate. Of course corrosive or irritant salts should be avoided. Oxidising salts such as persulphates, which have been proposed as components of animal litter in virtue of their reactivity with animal dross, are unnecessary. Preferably two or more salts are present, at least one of which is an alkali metal carbonate, especially when used as a clay activator.

If the litter is to lie in open atmosphere for a substantial time, the water-soluble component should not be deliquescent at the relative humidity at which it is to be used. If the litter is to be used at will by an animal, the non-clay component should not have a feel or smell offensive to the animal at the content used.

The non-clay content of the composition should be sufficient to cause rapid disintegration of the granules or agglomerates thereof when contacted with excess water. Usually 0.5 to 10.0, preferably 1 to 5, % in total, is an effective content of water-soluble non-clay component. The content of water-insoluble non-clay component is preferably in the range 5 to 20%. If the non-clay component is a water soluble salt, its concentration should be kept to about the minimum effective, both on economic grounds and because high concentrations inhibit redispersion or cause flocculation. This applies especially if salt having one or both ions of valency 2 or more is present.

As finely divided water insoluble non-clay component there may be used for example calcium carbonate, magnesium carbonate, dolomite or calcium phosphate. Other examples include pulverised fly ash.

The composition may contain minor components such as oil, pigment, scent, polymer or surfactant. Some of such materials may enter as impurities or additives in the salt used, for example crystal modifier such as sodium ferrocyanide and/or anti-caking agent such as calcium phosphate and/or humectant such as glycerol in sodium chloride.

If the non-clay component is or includes surfactant, and/or surfactant auxiliary, dispersion of the agglomerates in the larger water addition is facilitated and the resulting dispersion is more stable.

The surfactant is preferably anionic or non-ionic, since cationics tend to form water-repellent films on ceramic surfaces commonly encountered in sewerage systems. If it is anionic it is preferably a sulphate or sulphonate, since these are less sensitive to calcium or magnesium ions in hard water.

Examples of anionics are:

- a C_{10-20} aliphatic hydrocarbon chain terminating in a sulphate or sulphonate group;
- a sulphonated aromatic ring carrying $C_{\theta-20}$ alkyl group;

sulphated succinic esters such as dioctyl sodium

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succinate;

naphthalene sulphonic acids, especially their formaldehyde condensates, for example 'Dispersol L';

Other usable anionics are salts of C₁₂₋₂₀carboxylic acids, such as common soap (sodium stearate or palmitate) and sarcosine carrying the radical of such carboxylic acids. A water-softening additive may be desirable to assist redispersion in hard water.

Examples of non-ionics have C_{10-10} hydrocarbon chain linked directly or through phenyl to polyalkylene oxide.

Surfactant having both anionic and non-ionic groups can be used.

For convenience in mixing with clay, the surfactant is preferably one available in powdered solid form.

The surfactant auxiliary can be for example any of those proposed or used in detergent formulations for functions such a 'building', water-softening and soil dispersion. Thus soluble silicate 'builder' and/or polyphosphate or zeolite water-softener and/or polyphosphate can be used. Conveniently the surfactant and auxiliary can be introduced as a mixture as marketed for domestic or industrial use, provided it does not (for litter likely to contact human or animal skin) contain material that would be irritant at the concentrations used in the composition.

The content of surfactant is typically in the

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range 0.01 to 5%, especially 0.1 to 1%. The content of surfactant auxiliary is typically also in these ranges.

The invention provides also processes of making the composition by mixing the components.

Mixing should be in conditions affording the required association of the water-soluble component with the clay. For example, when the water-soluble component is a solid, such as a salt or surfactant, mixing is in presence of sufficient moisture to permit cohesion of the or other fine solid to the clay. The moisture content must evidently be less than would cause agglomeration of the clay. It is found in practice that apparently dry clay having a moisture content up to 15, conveniently in the range 5-12, %, supplies sufficient moisture. Salt and/or surfactant may be added as a solution if mixing is vigorous enough to disperse it quickly through the clay particles or if water is simultaneously dried off. Using apparently dry ingredients at least part of the necessary moisture may be supplied from the humidity of the atmosphere, either naturally or by added steam. Moisture may be supplied by using a salt carrying water of crystallisation, and/or by using salt that would in absence of clay be deliquescent, and/or using salt containing humectant.

The particle size of the clay ingredient is preferably substantially the same as intended for the composition and litter. If desired, the mixing stage

can agglomerate fines up to the intended particle size.

Thus dusty clay can be used as starting material. Too much size-enlargement would, however, necessitate subsequent grinding and sieving.

The non-clay component if solid is preferably at a smaller particle size than the clay ingredient, suitably 0.1 to 0.5mm. Larger particles would necessitate more vigorous mixing and/or using more water and running a greater risk of agglomeration. For surfactant the desired small particle size corresponds to a bulk density less than 0.4 g/ml.

As mixing apparatus any dry mixer can be used, conveniently a pan mixer or culinary mixer or concrete mixed or tumbling vessel mixer.

The invention provides a combination process comprising the stages:

- a) shearing and granulating raw wet clay at 25-35% water with sodium carbonate;
- b) drying the granules to 5-12% water and (if required) adjusting their particle size; and
- c) mixing the product of b) with at least hydrophilic component to a total content, including said sodium carbonate, in the range 0.5 to 10.0% if water-soluble or 5 to 20% if water-insoluble, said hydrophilic component having a particle size smaller than said granules.

The invention is illustrated but not limited by the following Examples.

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Example 1

The clay ingredient was a granulated >85% sodium bentonite sold under the Trade Name CULSEAL for use as a soil sealant eg. for waterproofing earth dams. Its composition was:

LOI SiO₂ Al₂O₃ Fe₂O₃ TiO₂ CaO MgO K_2 O Na₂O 7.71 63.5 15.9 2.87 0.47 2.23 3.4 0.72 3.52 (LOI = loss on ignition)

The Na_2O was to the extent of 1.1% derived from sodium carbonate added before wet granulation.

Exchangeable cations meq/100g Ca^{2*} 12.0

Mg²⁺ 50.0

Na* & K* 58.0

Bulk density tapped 100 g/cm³

Specific gravity 2.34

Moisture % 6-12

Screen analysis + 2000 micron 5% max

- 75 15% max

Swelling index 17 ml/2g.

The salt was sodium chloride in the form of caking-resistant cooking salt of average particle size about 0.5mm, and believed to contain fractional percentages of humectant and powdery anti-caking agent.

The ingredients (97 parts clay, 3 parts salt) were mixed dry in a KENWOOD culinary mixer until distinct particles of salt were no longer visible to the naked eye. This mixing did not noticeably break clay granules, but apparently caused some agglomeration into

granules of the fines initially present. The resulting composition was put into storage.

Test.

Half a litre of the composition was spread to a depth of 2cm in a plastics litter tray. Water (5 ml) was dripped on to each of two locations of the litter. To one location ten seconds later a sheet of filter paper was applied, held down for 20 sec by means of a 200g weight, then removed; no wet clay adhered to the paper. The clay at the other location was, after 10-15 seconds, found to be agglomerated to a lump about 2.5cm in diameter. The lump was lifted out without peripheral breakage using a house-plant fork and left overnight in ambient conditions. Next day it was drowned into 2 litres of water containing hypochlorite disinfectant in a bucket, stirred with a plastic paddle, allowed to settle for about 1 min and poured off. The poured-off liquid was a stable milky dispersion and was flushed away down a toilet pedestal without leaving visible residue. Almost no solid residue was left in the bucket; this also was flushed away with the aid of more disinfected water.

Example 2

- a) Example 1 was repeated except for using 10% of finely powdered calcium carbonate (90% CaCO₃, 5% moisture; 90% under 1mm, 60% under 0.6mm) in addition to the sodium chloride.
 - b,c) Example 2 a) was repeated using the calcium

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carbonate but no sodium chloride, and also using dolomite (under 0.8mm).

The test results were substantially the same as in Example 1. Despite being insoluble in water, the calcium carbonate was at the drowning stage stably enough dispersed to leave only a small residue, and the dispersion was toilet-flushed without blockage.

Examples 3-5

The clay ingredient, mixing procedure and test procedure were as described in Example 1. The following compositions were made and tested:

3a,b,c: a range of percentages of sodium C_{12-18} sulphate ('EMPICOL LX' ex Albright & Wilson; this was a finely divided material of relative density 0.22). The times to incipient visible break-up of agglomerate in still water were:

- % EMPICOL 0.1 0.3 1.0 time (sec) 50 25 9
- 4. Examples 3a-c were repeated but with also 3% sodium chloride present in each composition. The incipient break-up times were approximately half those noted for the compositions of Examples 3a-c. These are to be compared with 15-20 sec for compositions as in Example 1 containing 3% sodium chloride but no surfactant.
- 5. The composition contained 97 clay, 3 sodium chloride, and 0.6 'PERSIL automatic' non-biological machine washing powder containing sodium perborate,

phosphate water-softener, polymer/polycarboxylate dispersant, sodium carbonate and silicate and sodium sulphate. (It also contained brightening agents and perfume believed to be irrelevant to animal litter use).

In each Example using surfactant it was noted that the redispersed agglomerate, on standing for 10 min, settled out less than when surfactant was not used. Each agglomerate containing salt and/or surfactant redispersed well in water whether or not hypochlorite was present; and each was toilet-flushed without blockage. Redispersion took place satisfactorily in water hardened by a trace of magnesium sulphate. A representative sample of each was used by a cat without apparent objection or adhesion to the cat's fur and paws. No development of odours was observed.

CLAIMS

- 1. A litter box charged with a flowable granular composition convertible in contact with a small water addition to agglomerates readily dispersible in a large water addition comprising at least one water-swellable clay mineral and at least one hydrophilic non-clay component additional to any alkali bound to the clay.
- 2. A litter box according to claim 1 in which said component is at least one of a non-surfactant water-soluble material, a water-soluble surfactant and a finely divided water-insoluble surfactant and a finely divided water-insoluble material.
- 3. A litter box according to claim 1 or claim 2 in which in the composition the balance between cohesiveness of said agglomerates and redispersibility thereof is adjusted in favour of redispersibility by inclusion of the said non-clay component.
- 4. A litter box according to any one of the preceding claims in which the clay mineral is rapidly swollen by water to 5-10 ml water per g within 3 minutes to a coherent gel.
- 5. A litter box according to any one of the preceding claims in which the clay mineral is over 50, more preferably over 65, especially over 80, % w/w sodium bentonite.
- 6. A litter box according to any one of the preceding claims in which the non-clay component is present as solid particles adherent to the exterior of

the clay mineral particles.

- 7. A litter box according to any one of the preceding claims in which the clay mineral is at least 50% the product of wet extrusion.
- 8. A litter box according to any one of the preceding claims in which the clay mineral is an opened clay mineral that has been subjected to treatment in presence of water in shearing conditions in presence of mild alkali.
- 9. A litter box according to any one of the preceding claims in which the clay mineral is the product of a process in which raw sodium bentonite is activated with soda ash, milled in a pan muller, extruded through slots in the pan floor, then dried and screened.
- 10. A litter box according to any one of the preceding claims in which the non-clay component is or includes one or more salts having a solubility of at least 4, especially at least 20, g per 100ml of water at ambient temperature and has the anion preferably of an acid at least as strong as acetic acid.
- 11. A litter box according to claim 10 in which the salt component is uni-univalent.
- 12. A litter box according to any one of the preceding claims in which the non-clay content of the composition is in the range 0,5 to 10.0, preferably 1 to 5,% in total if water-soluble and 5 to 20% if water-insoluble.

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- 13. A litter box according to any one of claims 1 to 9 and 12 in which the non-clay component is a finely divided water insoluble material and is one or more of calcium carbonate, magnesium carbonate, dolomite, calcium phosphate and pulverised fly ash.
- 14. A litter box according to any one of the preceding claims in which the non-clay component is or includes an anionic and/or non-ionic surfactant.
- 15. A litter box according to claim 14 in which the surfactant is a sulphate or sulphonate.
- 16. A litter box according to any one of the preceding claims in which the non-clay component is or includes a surfactant auxiliary.
- 17. A litter box according to any one of claims 1 to 11 and 18 to 21 in which the content of surfactant is in the range 0.01 to 5%, especially 0.1 to 1%.
- 18. Composition comprising at least one water-swellable clay mineral and at least one hydrophilic non-clay component additional to any alkali bound to the clay, characterised in that the non-clay component is present as solid particles adherent to the exterior of the clay particles.
- 19. Composition according to claim 18 having any one or more of the preferred features set out in claims 1 to 17.
- 20. A process of making the composition according to claim 18 or 19 by mixing the components in presence of sufficient moisture to permit adhesion of finely

divided solid non-clay component to the clay mineral particles.

- 21. A process according to claim 20 in which the clay particles are apparently dry having a moisture content up to 15, conveniently in the range 5-12,% and the non-clay component is at a smaller particle size than the clay ingredient, suitably 0.1 to 0.5mm.
- 22. A process according to claim 20 or claim 21 comprising the stages:
- a) shearing and granulating raw wet clay at 25-35% water with sodium carbonate;
- b) drying the granules to 5-12% water and (if required) adjusting their particle size; and
- c) mixing the product of b) with at least hydrophilic component to a total content, including said sodium carbonate, in the range 0.5 to 10.0% if water-soluble or 5 to 20% if water-insoluble, said hydrophilic component having a particle size smaller than said granules.
- 23. A process of handling water-wet animal dross which comprises contacting it with a litter box according to any one of claims 1 to 17 and removing the resulting agglomerates selectively.
- 24. A process according to claim 23 including the further steps of redispersing said agglomerate in excess water and disposing of said redispersed material by sewer.

INTERNATIONAL SEARCH REPORT

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		NO-B- US-A-	175181 5317990	07-06-94
		AU-B-	639321	22-07-93
		AU-B-	7590691	16-01-92
		CA-A-	2045105	17-01-92
US-A-4570573	18-02-86	NONE		
US-A-5109804	05-05-92	NONE		
US-A-4278047	14-07-81	NONE		
EP-A-573303	08-12-93	NONE		